

COSMETIC COMPOSITIONS WITH SILICONE RESIN POLYMERS

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Technical Field

The invention is in the field of cosmetic compositions for application to skin, hair, or nails.

Background of the Invention

Cosmetics companies are on an eternal quest to develop products with improved
10 properties. Wear is one very important property of a cosmetic. Consumers want cosmetics, especially color cosmetics, to stay on the keratinous surface to which they are applied for the desired amount of time, and at the same time be readily removable from the keratinous surface when the consumer wants. With respect to certain color cosmetics such as lipsticks, wear is particularly important. Women want a lipstick to be comfortable and wear a reasonably long
15 time so that frequent reapplications are not necessary.

It is well known that certain silicone resins referred to as "MQ resins" or "MT resins" provide cosmetics with exceptional wear. Use of such resins in cosmetic compositions is well known. U.S. Patent No. 5,800,816 teaches a wide variety of cosmetic compositions containing a certain type of MQ resin (also referred to as trimethylated silica or trimethylsiloxy silicate). The
20 particular MQ resin taught in the '816 patent is, preferably, a high molecular weight particulate material that is generally known to be a hard resin. This hardness may cause certain cosmetics containing the resin to exhibit a grittiness, which can sometimes be ameliorated by solvating the resin in various silicone solvents.

It has been discovered that the properties of MQ and MT resins can be tailored by varying the ratio of M to Q units in the final polymer or, in the case of MT resins, the ratio of M to T units in the final polymer. Hardness, in particular, is one property that can be affected by varying M, Q, and T ratios in the polymer. In particular, it has been discovered that MQ and MT resins exhibiting a very specific hardness (and ratio of M to Q or M to T units) is especially desired for use in long wearing or transfer resistant cosmetic compositions. These desired resins are either of medium hardness, or soft, and when used in cosmetic compositions provide excellent long wearing properties. Most unexpectedly, they provide the additional, and very coveted, benefit of providing a non-matte, shiny finish. While the traditionally used "hard" MQ resins similarly provide excellent long wear or transfer resistant properties they tend to provide a very matte texture.

Accordingly, it is an object of the invention to provide cosmetic compositions containing silicone resins having a certain specific ratio of M, Q, or T units.

It is a further object of the invention to provide cosmetic compositions that are long wearing, or transfer resistant, and shinier, containing certain silicone resins which have specified ratios of units in the polymer.

It is a further object of the invention to provide a method for improving the long wear or transfer resistant properties of a cosmetic composition by formulating said composition with silicone resins containing a certain ratio of M, Q, or T units in the polymer.

Summary of the Invention

The invention is directed to a cosmetic composition containing a silicone resin comprised of M units in combination with Q or T units or both, wherein the number of M units is greater than, up to about three times more, than the number of Q units or T units or combination thereof.

The invention is directed to a method for improving the finish of a cosmetic composition by formulating such composition with a silicone resin comprised of M units in combination with Q or T units or both, wherein the number of M units in the polymer is greater than, or up to about three times more, than the number of Q or T units or combination thereof.

Detailed Description

All percentages referred to herein are percentages by weight unless otherwise indicated.

I. The Cosmetic Compositions

A. The Silicone Resin Polymer

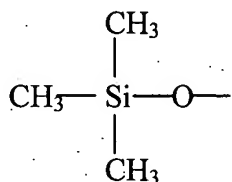
The cosmetic compositions of the invention comprise a silicone resin polymer having M units and T or Q units or both, wherein the number of M units in the polymer is equal to, or greater than, the number of Q units or T units or combination thereof. Preferably the silicone resin polymer is present in the compositions in amounts ranging from about 0.01-95%, preferably about 0.05-80%, more preferably about 0.5-50% by weight of the total composition.

The term "M" means "monofunctional", and refers to a siloxy unit that contains one silicon atom bonded to one oxygen atom, with the remaining three substituents on the silicon atom being other than oxygen. In particular, in a monofunctional siloxy unit, the oxygen atom present is shared by 2 silicon atoms when the monofunctional unit is polymerized with one or more of the other units. In silicone nomenclature used by those skilled in the art, the monofunctional siloxy unit is designated by the letter "M", and means a unit having the general formula:



wherein R_1 , R_2 , and R_3 are each independently C_{1-30} , preferably C_{1-10} , more preferably

C₁₋₄ straight or branched chain alkyl, which may be substituted with phenyl or one or more hydroxyl groups; phenyl; alkoxy (preferably C₁₋₂₂, more preferably C₁₋₆); hydroxyl; or hydrogen. The SiO_{1/2} designation means that the oxygen atom in the monofunctional unit is bonded to, or shared, with another silicon atom when the monofunctional unit is polymerized with one or more of the other types of units. For example, when R₁, R₂, and R₃ are methyl the resulting monofunctional unit is of the formula:



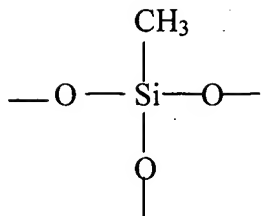
When this monofunctional unit is polymerized with one or more of the other units the oxygen atom will be shared by another silicon atom, i.e. the silicon atom in the monofunctional unit is bonded to ½ of this oxygen atom.

The term "T" in silicone nomenclature means "trifunctional" and refers to a trifunctional siloxy unit.

A "T" unit has the general formula:



wherein R₁ is as defined above. The SiO_{3/2} designation means that the silicon atom is bonded to three oxygen atoms when the unit is copolymerized with one or more of the other units. For example when R₁ is methyl the resulting trifunctional unit is of the formula:

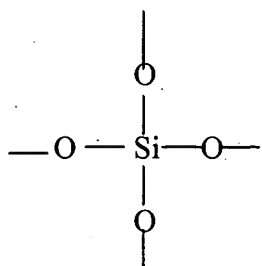


When this trifunctional unit is polymerized with one or more of the other units, the silicon atom shares three oxygen atoms with other silicon atoms, i.e. will share three halves of an oxygen atom.

The term "Q" means "tetrafunctional" with respect to a siloxy unit. A "Q" unit has the general formula:



The $\text{SiO}_{4/2}$ designation means that the silicon shares four oxygen atoms (i.e. four halves) with other silicon atoms when the tetrafunctional unit is polymerized with one or more of the other units. The $\text{SiO}_{4/2}$ unit is best depicted as follows:

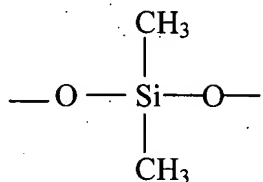


The silicone resin polymers used in the composition of the invention may also contain other units such as "D" units, in addition to the M, T, and Q units described above.

The term "D" in standard silicone nomenclature means "difunctional" with respect to a siloxy unit. If the D unit is substituted with substituents other than methyl the "D" designation is sometimes used, which indicates a substituent other than methyl. For purposes of this disclosure, a "D" unit has the general formula:



wherein R_1 and R_2 are defined as above. The $SiO_{2/2}$ designation means that the silicon atom in the difunctional unit is bonded to two oxygen atoms when the unit is polymerized with one or more of the other units. For example, when R_1 , R_2 , are methyl the resulting difunctional unit is of the formula:



When this difunctional unit is polymerized with one or more of the other units the silicon atom will be bonded to two oxygen atoms, i.e. will share two one-halves of an oxygen atom.

The silicone resin polymer used in the compositions of the invention may be a combination of M and Q units, a combination of M and T units, a combination of M and Q + T units, or all three of such combinations additionally containing one or more "D" units, so long as the number of M units in the silicone resin polymer is greater than the number of T units, Q units, D units, or combination thereof. Preferably, the silicone resin polymer used in the compositions of the invention contains M units which are greater than, up to three times greater, than the number of Q units, T units, D units, or combinations thereof. More preferably, the number of M units is greater than, up to two and a half times greater, than the number of Q units, T units, D units, or combinations thereof. Most preferred is where the silicone resin polymer is

an MQ resin and the number of M units is greater than about 1.5 times, and up to three times, greater than the number of Q units in the polymer. Other types of silicone resin polymers that may be used in the compositions of the invention include, but are not limited to polymers comprising:

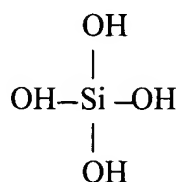
- 5 (1) M and Q units where the number of M units is about 1.1 times greater than the number of Q units (e.g. for every 1.1 M units there are 1.0 Q units)
- (2) M and Q units where the number of M units is about twice the number of Q units
- (3) M and Q units where the number of M units is about two and a half times the number of Q units
- 10 (4) M and Q units where the number of M units is about one and a half times the number of Q units
- (5) M and Q units where the number of M units is about three times the number of Q units
- (6) M, Q, and T units where the number of M units is about 1.1 times the number of Q+T units
- (7) M, Q, and T units where the number of M units is about three times greater than the number
- 15 of Q+T units
- (8) M, Q, and T units where the number of M units is about two times the number of Q+T units
- (9) M, Q, and T units where the number of M units is about two and a half times the number of Q+T units
- (10) M, Q, and T units where the number of M units is about one and a half times the number of
- 20 Q+T units

All of the combinations mentioned above, where one or more D units are additionally present, preferably in minor amounts and the number of M units is in the ratio specified when compared to the number of Q+T+D units. By way of illustration, for (10) above, the number of

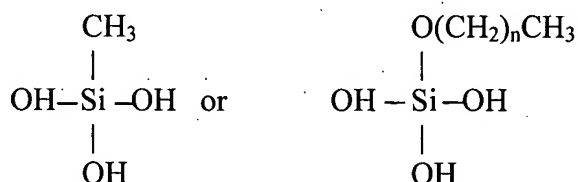
M units is about one and a half times the number of Q+T+D units. The ranges mentioned above include all numerical values within the range from "greater than 1" to "about three" times, including but not limited to values such as 1.1, 1.2, 1.3, 1.4, 1.6, 1.7, 1.8, 1.9, 2.1, 2.2, 2.3, 2.4, 2.6, 2.7, 2.8, 2.9, etc. With respect to the previous sentence, by way of illustration, in a polymer having M and Q units, where the number of M units is about 1.6 times the number of Q units, or for every 1.6 M units there is about 1 Q unit.

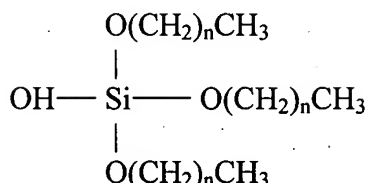
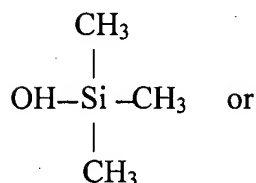
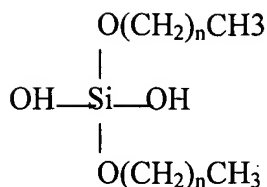
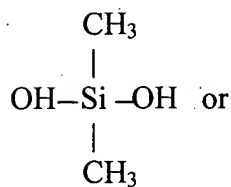
The silicone resin polymer is preferably a film forming and may be a liquid, semi-solid, or solid at room temperature.

The silicone resin polymer used in the compositions of the invention are made according to processes well known in the art. In general siloxane polymers are obtained by hydrolysis of silane monomers, preferably chlorosilanes. The chlorosilanes are hydrolyzed to silanols and then condensed to form siloxanes. For example, Q units are often made by hydrolyzing tetrachlorosilanes in aqueous or aqueous/alcoholic media to form the following:



The above hydroxy substituted silane is then condensed or polymerized with other types of silanol substituted units including but not limited to those such as:





wherein n is 0-10, preferably 0-4.

Because the hydrolysis and condensation may take place in aqueous or aqueous/alcoholic media wherein the alcohols are preferably lower alkanols such as ethanol, propanol, or isopropanol, the units may have residual hydroxyl or alkoxy functionality as depicted above.

Preferably, the resins are made by hydrolysis and condensation in aqueous/alcoholic media, which provides resins that have residual silanol and alkoxy functionality. In the case where the alcohol is ethanol, the result is a resin that has residual hydroxy or ethoxy functionality on the siloxane polymer. The silicone film forming polymers used in the compositions of the invention are generally made in accordance with the methods set forth in Silicon Compounds (Silicones), Bruce B. Hardman, Arnold Torkelson, General Electric Company, Kirk-Othmer Encyclopedia of Chemical Technology, Volume 20, Third Edition, pages 922-962, 1982, which is hereby incorporated by reference in its entirety.

B. Other Ingredients.

The silicone resin polymer may be incorporated into a wide variety of cosmetic compositions for skin, nails, or hair, such as lotions, creams, gels, shampoos, hair conditioners,

sprays, mousses; color cosmetics such as mascara, eyeshadow, blush, eyeliner, brow color, foundation, concealer, lipstick, lipliner, and so on. The compositions may be in the anhydrous or water and oil emulsion form. If the latter, the emulsions may be water-in-oil or oil-in-water.

Generally emulsions comprise from about 0.1-95%, preferably about 0.1-85%, preferably about 1-75% water and about 0.1-95%, preferably about 0.1-85%, more preferably about 1-75% oil.

Examples of such other ingredients include, but are not limited to, those set forth herein.

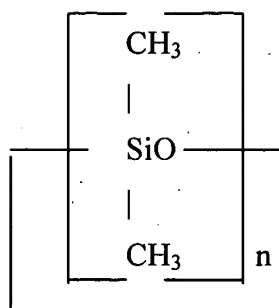
1. Oils

Whether in the emulsion or anhydrous form, the compositions of the invention may comprise one or more oils. The term "oil" in the context of this invention means an animal, vegetable, mineral, synthetic, or silicone oil that is liquid or semi-solid at room temperature. The oil may be volatile or non-volatile. The term "volatile" means that the oil has a vapor pressure of greater than about 2 mm. of mercury at 20° C. The term "non-volatile" means that the oil has a vapor pressure of less than about 2 mm. of mercury at 20° C. If present, suggested ranges of oil found in the compositions of the invention are from about 0.1-80%, preferably about 0.5-75%, more preferably about 1-70% by weight of the total composition. Examples of oils suitable for use in the composition include, but are not limited to those set forth herein.

(a). Silicone Oils

Suitable silicone oils include volatile linear or cyclic silicones. Generally such silicones have a viscosity ranging from about 0.1 to 10 centistokes at 25° C. If present, suggested ranges of volatile silicone are from about 0.1-80%, preferably about 0.5-75%, more preferably about 1-65% by weight of the total composition.

Cyclic silicones (or cyclomethicones) are of the general formula:



where $n = 3-6$.

10 Linear volatile silicones that may be used in the compositions of the invention generally having the formula:



where $n=0-7$, preferably 0-5, more preferably 1-4. Examples of such linear volatile silicones include hexamethyldisiloxane, octamethyltrisiloxane, decamethyltetrasiloxane,

15 dodecamethylpentasiloxane, and mixtures thereof.

Linear and cyclic volatile silicones are available from various commercial sources including Dow Corning Corporation and General Electric. The Dow Corning volatile silicones are sold under the tradenames Dow Corning 244, 245, 344, and 200 fluids. These fluids comprise octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, cyclohexasiloxane, and
20 mixtures thereof.

Also suitable for use in the compositions of the invention are various non-volatile silicone oils, both water soluble and water insoluble. Such silicones preferably have a viscosity ranging from about 5 to 1,000,000 centipoise, preferably 10 to 700,000 centipoise at 25° C. Suitable water insoluble silicones include amine functional silicones such as amodimethicone; phenyl

substituted silicones such as phenyl trimethicone, phenyl dimethicone, dimethicone, dimethiconol, C₁₋₃₀ alkyl substituted dimethicones such as cetyl dimethicone, isostearyl dimethicone, and the like. These types of silicones are available from a variety of sources including Dow Corning Corporation, GE Silicones, Wacker, and the like.

5 Water soluble or dispersible silicones such as dimethicone copolyol, dimethiconol, or alkyl dimethicone copolyols (for example cetyl dimethicone copolyol), and similar, may also be used. Such silicones are available from Dow Corning as the 3225C formulation aid, Dow 190 and 193 fluids, or similar products marketed by Goldschmidt under the ABIL tradename.

(b). Hydrocarbons

10 The oil may comprise one or more volatile or non-volatile hydrocarbon oils. Examples of volatile hydrocarbons include various straight or branched chain paraffinic hydrocarbons having 5 to 40 carbon atoms, more preferably 8-16 carbon atoms. Suitable hydrocarbons include pentane, hexane, heptane, octane, decane, dodecane, tetradecane, tridecane, and C₈₋₂₀ isoparaffins such as isododecane, isohexadecane, and those disclosed in U.S. patent nos. 3,439,088 and
15 3,818,105, both of which are hereby incorporated by reference. Preferred volatile paraffinic hydrocarbons have a molecular weight of about 70-225, preferably about 160 to 190 and a boiling point range of 30 to 320°, preferably 60-260° C., and a viscosity of less than about 10 centipoise at 25° C. Such paraffinic hydrocarbons are available from EXXON under the ISOPARS trademark, and from the Permethyl Corporation.

20 Suitable nonvolatile hydrocarbon oils include longer chain isoparaffins and olefins, preferably those having greater than about 18 to 20 carbon atoms. Examples of such hydrocarbon oils include C₂₄₋₂₈ olefins, C₃₀₋₄₅ olefins, C₂₀₋₄₀ isoparaffins; polyisobutene,

polydecene, polybutene, and hydrogenated derivatives thereof; mineral oil, pentahydrosqualene, squalene, squalane, and mixtures thereof.

Also suitable are lower organic liquids including saturated or unsaturated, substituted or unsubstituted branched or linear or cyclic organic compounds that are liquid under ambient conditions. Preferred organic liquids include those described in U.S. Patent No. 5,505,937; 5,725,845; 5,019,375; and 6,214,329, all of which are incorporated by reference herein in their entirety. Such silicones or organic oils include those further described as follows:

(c). Esters

Suitable esters that may be used in the compositions of the invention are mono-, di-, and triesters. The composition may comprise one or more esters selected from the group, or mixtures thereof.

(i). Monoesters

Monoesters are defined as esters formed by the reaction of a monocarboxylic acid having the formula $R-COOH$, wherein R is a straight or branched chain saturated or unsaturated alkyl having 2 to 50 carbon atoms, or phenyl; and an alcohol having the formula $R-OH$ wherein R is a straight or branched chain saturated or unsaturated alkyl having 2-50 carbon atoms, or phenyl.

Both the alcohol and the acid may be substituted with one or more hydroxyl groups, or may contain other groups such as ester, ether, and the like. Either one or both of the acid or alcohol may be a "fatty" acid or alcohol, and may have from about 6 to 30 carbon atoms. Examples of

monoester oils that may be used in the compositions of the invention include hexyldecyl benzoate, hexyl laurate, hexadecyl isostearate, hexyldecyl laurate, hexyldecyl octanoate, hexyldecyl oleate, hexyldecyl palmitate, hexyldecyl stearate, hexyldodecyl salicylate, hexyl isostearate, butyl acetate, butyl isostearate, butyl oleate, butyl octyl oleate, cetyl palmitate, cetyl

octanoate, cetyl laurate, cetyl lactate, isostearyl isononanoate, cetyl isononanoate, cetyl stearate, stearyl lactate, stearyl octanoate, stearyl heptanoate, stearyl stearate, and so on. It is understood that in the above nomenclature, the first term indicates the alcohol and the second term indicates the acid in the reaction, i.e. stearyl octanoate is the reaction product of stearyl alcohol and octanoic acid.

(ii). Diesters

Suitable diesters that may be used in the compositions of the invention are formed by the reaction of a dicarboxylic acid and an aliphatic or aromatic alcohol, or the reaction of an aliphatic or aromatic alcohol having at least two hydroxyl groups with one or more carboxylic acids. The dicarboxylic acid may contain from 2 to 50 carbon atoms, and may be in the straight or branched chain, saturated or unsaturated form. The dicarboxylic acid may be substituted with one or more hydroxyl groups. The aliphatic or aromatic alcohol may also contain 2 to 50 carbon atoms, and may be in the straight or branched chain, saturated, or unsaturated form. The aliphatic or aromatic alcohol may be substituted with one or more substituents such as hydroxyl. Preferably, one or more of the acid or alcohol is a fatty acid or alcohol, i.e. contains 14-22 carbon atoms. The dicarboxylic acid may also be an alpha hydroxy acid. Examples of diester oils that may be used in the compositions of the invention include diisostearyl malate, esters of neopentyl glycol such as neopentyl glycol dioctanoate, dibutyl sebacate, di-C₁₂₋₁₃ alkyl malate, dicetearyl dimer dilinoleate, dicetyl adipate, diisocetyl adipate, diisononyl adipate, diisostearyl dimer dilinoleate, disostearyl fumarate, diisostearyl malate, and so on.

(iii). Triesters

Suitable triesters comprise the reaction product of a tricarboxylic acid and an aliphatic or aromatic alcohol, or alternatively, the reaction of an aliphatic or aromatic alcohol having at least

three hydroxyl groups with one or more carboxylic acids. As with the mono- and diesters mentioned above, the acid and alcohol contain 2 to 30 carbon atoms, and may be saturated or unsaturated, straight or branched chain, and may be substituted with one or more hydroxyl groups. Preferably, one or more of the acid or alcohol is a fatty acid or alcohol containing 14 to 22 carbon atoms. Examples of triesters include triarachidin, tributyl citrate, triisostearyl citrate, tri C₁₂₋₁₃ alkyl citrate, tricaprylin, tricaprylyl citrate, tridecyl behenate, trioctyldodecyl citrate, tridecyl behenate, tridecyl cocoate, tridecyl isononanoate, and so on.

(iv). Tetraesters

Suitable tetraesters comprise the reaction product of alcohols having four hydroxyl groups such as pentaerythritol, with carboxylic acids which may be the same or different, and as described above with respect to the mono-, di-, and triesters. Examples of such tetraesters include esters of pentaerythritol and C₁₋₃₀ monocarboxylic acids. All of the hydroxyl groups may be reacted with monocarboxylic acids, or only one, two, or three.

(d). Lanolin Oil

Also suitable for use in the composition is lanolin oil or derivatives thereof containing hydroxyl, alkyl, or acetyl groups, such as hydroxylated lanolin, isobutylated lanolin oil, acetylated lanolin, acetylated lanolin alcohol, and so on.

(e). Glyceryl Esters of Fatty Acids

The nonvolatile oil may also comprise naturally occurring or synthetic glyceryl esters of fatty acids, or triglycerides. Both vegetable and animal sources may be used. Examples of such oils include castor oil, C₁₀₋₁₈ triglycerides, caprylic/capric/triglycerides, coconut oil, corn oil, cottonseed oil, linseed oil, mink oil, olive oil, palm oil, illipe butter, rapeseed oil, soybean oil, sunflower seed oil, walnut oil, and the like.

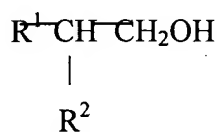
Also suitable are synthetic or semi-synthetic glyceryl esters, e.g. fatty acid mono-, di-, and triglycerides which are natural fats or oils that have been modified, for example, acetylated castor oil, or mono-, di- or triesters of polyols such as glyceryl stearate, diglyceryl diiosostearate, polyglyceryl-4 isostearate, polyglyceryl-6 ricinoleate, glyceryl dioleate, glyceryl diisostearate, glyceryl trioctanoate, diglyceryl distearate, glyceryl linoleate, glyceryl myristate, glyceryl isostearate, PEG castor oils, PEG glyceryl oleates, PEG glyceryl stearates, PEG glyceryl tallowates, and so on.

(f). Fluorinated Oils

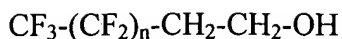
Also suitable as for use in the composition are various fluorinated oils such as fluorinated silicones, fluorinated esters, or perfluoropolyethers. Particularly suitable are fluorosilicones such as trimethylsilyl endcapped fluorosilicone oil, polytrifluoropropylmethoxysiloxanes, and similar silicones such as those disclosed in U.S. patent no. 5,118,496 which is hereby incorporated by reference.

Perfluoropolyethers like those disclosed in U.S. patent nos. 5,183,589, 4,803,067, 5,183,588 all of which are hereby incorporated by reference, which are commercially available from Montefluos under the trademark Fomblin.

Fluoroguerbet esters are also suitable oils. The term "guerbet ester" means an ester that is formed by the reaction of a guerbet alcohol having the general formula:

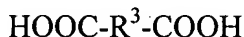


and a fluoroalcohol having the following general formula:



wherein n is from 3 to 40.

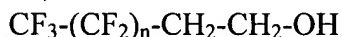
with a carboxylic acid having the general formula:



wherein R^1 , R^2 , and R^3 are each independently a straight or branched chain alkyl.

The guerbet ester may be a fluoro-guerbet ester which is formed by the reaction of a guerbet alcohol and carboxylic acid (as defined above), and a fluoroalcohol having the following

10 general formula:



wherein n is from 3 to 40.

Examples of suitable fluoro guerbet esters are set forth in U.S. patent no. 5,488,121, which is hereby incorporated by reference. Suitable fluoro-guerbet esters are also set forth in U.S. patent no. 5,312,968, which is hereby incorporated by reference.

2. Natural or Synthetic Waxes

A variety of waxes may be used in the compositions of the invention including animal, vegetable, mineral, or silicone waxes. If present in the composition, the waxes may range from about 0.1-50%, preferably about 0.5-40%, more preferably about 1-38% by weight of the total composition. Generally such waxes have a melting point ranging from about 28 to 125° C., preferably about 30 to 100° C. Examples of animal, vegetable, or mineral waxes include acacia, beeswax, ceresin, cetyl esters, flower wax, citrus wax, carnauba wax, jojoba wax, japan wax,

polyethylene, microcrystalline, rice bran, lanolin wax, mink, montan, bayberry, ouricury, ozokerite, palm kernel wax, paraffin, avocado wax, apple wax, shellac wax, clary wax, spent grain wax, candelilla, grape wax, and polyalkylene glycol derivatives thereof such as PEG6-20 beeswax, or PEG-12 carnauba wax.

5 Also suitable are various types of ethylene homo- or copolymeric waxes such as polyethylene (also referred to as synthetic wax), polypropylene, and mixtures thereof.

Also suitable are various types of silicone waxes, referred to as alkyl silicones, which are polymers that comprise repeating dimethylsiloxo units in combination with one or more methyl-long chain (C₁₆₋₃₀) alkyl units where the long chain alkyl is preferably a fatty chain that provides
10 a wax-like characteristic to the silicone. Such silicones include, but are not limited to stearoxydimethicone, behenoxy dimethicone, stearyl dimethicone, cetearyl dimethicone, cetyl dimethicone, and so on. Suitable waxes are set forth in U.S. Patent No. 5,725,845, which is hereby incorporated by reference in its entirety.

3. Rheological Additives

15 The compositions of the invention may comprise one or more rheological additives. The term "rheological additive" means an ingredient or combination of ingredients that increase the viscosity of, or thicken, the composition, and if particulates are present, may also suspend the particulates in the composition. If a rheological additive is present, most desired is one that is a non-matting rheological additive, which means that it exhibits a reduced tendency to mute or
20 matte the shininess of the silicone resin polymer. Suggested ranges of rheological additive are from about 0.01-60%, preferably about 0.05-50%, more preferably about 0.1-45% by weight of the total composition.

One type of non-matting rheological additive comprises natural or synthetic montmorillonite minerals such as hectorite, bentonite, and quaternized derivatives thereof which are obtained by reacting the minerals with a quaternary ammonium compound, such as stearalkonium bentonite, hectorites, quaternized hectorites such as Quaternium-18 hectorite, attapulgite, bentones, and the like. Another example of such a rheological additive is silicate metal silicate gelling agents, such as those sold under the tradename Laponite®.

Also suitable as rheological additives are various polymeric compounds known in the art as associative thickeners. Suitable associative thickeners generally contain a hydrophilic backbone and hydrophobic side groups. Examples of such thickeners include polyacrylates with hydrophobic side groups, cellulose ethers with hydrophobic side groups, polyurethane thickeners. Examples of hydrophobic side groups are long chain alkyl groups such as dodecyl, hexadecyl, or octadecyl; alkylaryl groups such as octylphenyl or nonylphenyl

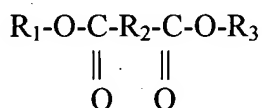
Another type of rheological additive that may be used in the compositions are silicas, silicates, silica silylate, and derivatives thereof. These silicas and silicates are generally found in the particulate form.

Also suitable as rheological additives are cross-linked organosiloxane compounds also known as silicone elastomers. Such elastomers are generally prepared by reacting a dimethyl methylhydrogen siloxane with a crosslinking group comprised of a siloxane having an alkylene group having terminal olefinic unsaturation or with an organic group having an alpha or omega diene. Examples of suitable silicone elastomers for use as rheological additives include Dow Corning 9040, sold by Dow Corning, and various elastomeric silicones sold by Shin-Etsu under the KSG tradename including KSG 15, KSG 16, KSG 19 and so on.

4. Plasticizers

It may also be desirable to include plasticizers in the compositions of the invention.

Plasticizers may improve the spreadability and application of the composition to the surface to which it is applied and in some cases will interact with the film forming polymer to make it more flexible. If present, the plasticizer may be found in the oil or water phase if the composition of the invention is in the form of an emulsion, and in the oil or lipophilic phase if the composition is in the anhydrous form. A variety of plasticizers are suitable including Suitable plasticizers include glyceryl, glycol, and citrate esters as disclosed in U.S. Patent No. 5,066,484, which is hereby incorporated by reference. Examples of such esters include glyceryl tribenzoate, glyceryl triacetate, acetyl tributyl citrate, dipropylene glycol dibenzoate, and the like. Also suitable, are plasticizers of the following general formula:



wherein R_1 , R_2 , and R_3 are each independently a C_{1-20} straight or branched chain alkyl or alkylene which may be substituted with one or more hydroxyl groups. Preferably, R_1 is a C_{3-10} straight or branched chain alkyl; R_2 is a C_{2-8} alkyl which may be substituted with one or more hydroxyl groups; and R_3 is a C_{3-10} straight or branched chain alkyl. Examples of such compounds include dioctyl malate, diisopropyl adipate, dibutyl adipate, dibutyl sebacate, dioactyl azelate, dioctyl succinate, dioctyl fumarate, and the like.

5. Particulates

The composition of the invention may contain one or more of a variety of particulates such as pigments, powders, or mixtures thereof. The particulate may be colored or non-colored (for example, white), and may have a particle size ranging from about 0.005 microns to 200 microns, preferably about 0.005 microns to 500 microns. If present, the particulate is preferably

present at ranges from about 0.001-95%, preferably about 0.005-90%, more preferably about 0.01-70% by weight of the total composition. Suitable particulates include organic and inorganic pigments, powders, or salts thereof.

Examples of suitable organic pigments include red, green, blue, yellow, violet, orange, and mixtures thereof. Also suitable are Lakes of such pigments, which means that the organic pigments are reacted with a metal salt such as calcium, aluminum, barium, zirconium, and the like to form salts. Particularly preferred are aluminum Lakes of the organic pigments, which is where the organic pigment is reacted with aluminum to form the aluminum salt. Formation of the metal salt of the organic pigment will generally also convert the pigment from a water soluble pigment into a water insoluble pigment, and such pigments tend to become even more lipophilic in nature, meaning that they will exhibit appreciable affinity for lipophilic or oily ingredients in the composition. Examples of organic pigment families that may be used herein include azo, (including monoazo and diazo), fluoran, xanthene, indigoid, triphenylmethane, anthroquinone, pyrene, pyrazole, quinoline, quinoline, or metallic salts thereof. Preferred are D&C colors, FD&C colors, or Lakes of D&C or FD&C colors. The term "D&C" means drug and cosmetic colors that are approved for use in drugs and cosmetics by the FDA. The term "FD&C" means food, drug, and cosmetic colors that are approved for use in foods, drugs, and cosmetics by the FDA. Certified D&C and FD&C colors are listed in 21 CFR 74.101 et seq. and include the FD&C colors Blue 1, Blue 2, Green 3, Orange B, Citrus Red 2, Red 3, Red 4, Red 40, Yellow 5, Yellow 6, Blue 1, Blue 2; Orange B, Citrus Red 2; and the D&C colors Blue 4, Blue 9, Green 5, Green 6, Green 8, Orange 4, Orange 5, Orange 10, Orange 11, Red 6, Red 7, Red 17, Red 21, Red 22, Red 27, Red 28, Red 30, Red 31, Red 33, Red 34, Red 36, Red 39, Violet 2, Yellow 7, Yellow 8, Yellow 10, Yellow 11, Blue 4, Blue 6, Green 5, Green 6, Green 8,

Orange 4, Orange 5, Orange 10, Orange 11, and so on. Suitable Lakes of D&C and FD&C colors are defined in 21 CFR 82.51. Particularly preferred are Lakes formed by the reaction of the organic pigment with a metallic salt such as aluminum, calcium, zirconium, barium, and the like. Suitable reds include pigments from the monoazo, disazo, fluoran, xanthene, or indigoid families or Lakes thereof, such as Red 4, 6, 7, 17, 21, 22, 27, 28, 30, 31, 33, 34, 36, and Red 40. Also suitable are Lakes of such red pigments. Typically the metal salts are aluminum, barium, and the like. Most preferred are Aluminum Lakes of the various red pigments mentioned herein.

Suitable yellows include wherein the yellow pigment is a pyrazole, monoazo, fluoran, xanthene, quinoline, or salt thereof. Suitable yellows include Yellow 5, 6, 7, 8, 10, and 11, as well as Lakes of such yellow pigments.

Suitable violets include those from the anthroquinone family, such as Violet 2 and Lakes thereof. Examples of orange pigments are Orange 4, 5, 10, 11, or Lakes thereof.

Also suitable are inorganic pigments that include iron oxides such as red, blue, black, green, and yellow; titanium dioxide, bismuth oxychloride, and the like. Preferred are iron oxides.

Examples of particulates that are filler-type materials that may be included in the composition include non-pigmentitious particles that generally have a particle size ranging from about 0.002 to 200, preferably 0.5 to 100, microns. Suitable particulate fillers include titanated mica, fumed silica, spherical silica, polymethylmethacrylate, micronized teflon, boron nitride, mica, acrylates copolymers, aluminum silicate, aluminum starch octenylsuccinate, bentonite, calcium silicate, cellulose, chalk, corn starch, diatomaceous earth, fuller's earth, glyceryl starch, hectorite, hydrated silica, kaolin, magnesium aluminum silicate, magnesium trisilicate, maltodextrin, montmorillonite, microcrystalline cellulose, rice starch, silk powder, silica, talc,

mica, zinc laurate, zinc myristate, zinc rosinate, alumina, attapulgite, calcium carbonate, calcium silicate, dextran, kaolin, nylon, silica silylate, sericite, soy flour, tin oxide, titanium hydroxide, trimagnesium phosphate, walnut shell powder, or mixtures thereof. The particulates may also be in the fiber form, such as cellulose fibers, rayon fibers, nylon or silk fibers and the like. Such fibers are generally circular in cross-section and have a discernable length. Preferably the length ranges from 1 to 5 mm.

The above mentioned pigments, powders or fibers may be inherently lipophilic, meaning that they are capable, alone, of being dispersed or solubilized in the oily or lipophilic phase of a cosmetic composition. The above mentioned pigments, powders, or fibers may also be inherently hydrophilic, meaning that they are capable, alone, of being dispersed or solubilized in the water phase or hydrophilic phase of a cosmetic composition. For example, certain types of organic pigments may be hydrophilic in nature and will be soluble or dispersible in water, however these pigments may, at the same time be dispersible in an oily phase. Further, in the case of organic pigments, such pigments may be reacted with metal salts to form Lakes, which cause the pigments to exhibit a more lipophilic character. In the compositions of the invention, the pigments may be inherently lipophilic or hydrophilic by virtue of surface treatments with lecithin, amino acids, mineral oil, silicone oil or various other agents either alone or in combination, which coat the particulate surface and render the particles more lipophilic in nature. The term "lipophilic" means that the pigment or particles will be solvated, dispersed, and/or compatible with the lipophilic or oily phase of the cosmetic composition. In the case of an emulsion, a lipophilic particle will have an affinity for the oily phase of the emulsion.

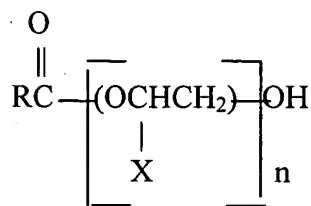
6. Surfactants

The compositions of the invention may comprise about 0.01-20%, preferably about 0.1-15%, more preferably about 0.5-10% by weight of the total composition of a surfactant.

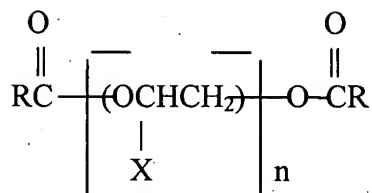
Surfactants may be used in both anhydrous and emulsion based compositions. The surfactant may be nonionic, although if the composition is in the form of a shampoo or conditioner it will preferably contain anionic or cationic surfactants, respectively.

Suitable nonionic surfactants or emulsifiers include alkoxyated alcohols, or ethers, formed by the reaction of an alcohol with an alkylene oxide, usually ethylene or propylene oxide. Preferably the alcohol is a fatty alcohol having 6 to 30 carbon atoms. Examples of such ingredients include Beheneth 5-30, which is formed by the reaction of behenyl alcohol and ethylene oxide where the number of repeated ethylene oxide units is 5 to 30; Cetareth 2-100, formed by the reaction of a mixture of cetyl and stearyl alcohol with ethylene oxide, where the number of repeating ethylene oxide units in the molecule is 2 to 100; Ceteth 1-45 which is formed by the reaction of cetyl alcohol and ethylene oxide, and the number of repeating ethylene oxide units is 1 to 45, and so on. Other alkoxyated alcohols are formed by the reaction of fatty acids and mono-, di- or polyhydric alcohols with an alkylene oxide. For example, the reaction products of C₆₋₃₀ fatty carboxylic acids and polyhydric alcohols which are monosaccharides such as glucose, galactose, methyl glucose, and the like, with an alkoxyated alcohol. Preferred are alkoxyated alcohols which are formed by the reaction of stearic acid, methyl glucose, and and ethoxyated alcohol, otherwise known as PEG-20 methyl glucose sesquiisostearate.

Also suitable as the nonionic surfactant are alkyoxylated carboxylic acids, which are formed by the reaction of a carboxylic acid with an alkylene oxide or with a polymeric ether. The resulting products have the general formula:

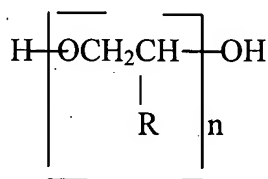


or



where RCO is the carboxylic ester radical, X is hydrogen or lower alkyl, and n is the number of polymerized alkoxy groups. In the case of the diesters, the two RCO- groups do not need to be identical. Preferably, R is a C₆₋₃₀ straight or branched chain, saturated or unsaturated alkyl, and n is from 1-100.

Also suitable as nonionic surfactants are monomeric, homopolymeric and block copolymeric ethers. Such ethers are formed by the polymerization of monomeric alkylene oxides, generally ethylene or propylene oxide. Such polymeric ethers have the following general formula:



wherein R is H or lower alkyl and n is the number of repeating monomer units, and ranges from 1 to 500.

Other suitable nonionic surfactants include alkoxyated sorbitan and alkoxyated sorbitan derivatives. For example, alkoxylation, in particular, ethoxylation, of sorbitan provides

polyalkoxylated sorbitan derivatives. Esterification of polyalkoxylated sorbitan provides sorbitan esters such as the polysorbates. Examples of such ingredients include Polysorbates 20-85, sorbitan oleate, sorbitan palmitate, sorbitan sesquiisostearate, sorbitan stearate, and so on.

Suitable cationic, anionic, zwitterionic, and amphoteric surfactants are disclosed in U.S.

5 Patent No. 5,534,265, which is hereby incorporated by reference in its entirety.

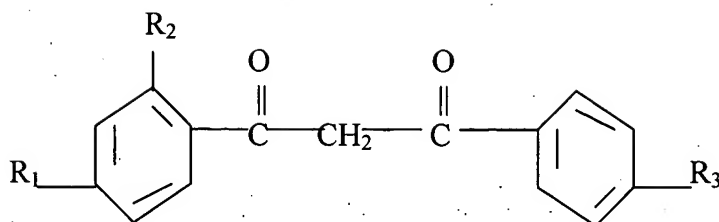
7. Sunscreens

If desired, the compositions of the invention may contain 0.001-20%, preferably 0.01-10%, more preferably 0.05-8% of one or more sunscreens. A sunscreen is defined as an ingredient that absorbs at least 85 percent of the light in the UV range at wavelengths from 290
10 to 320 nanometers, but transmits UV light at wavelengths longer than 320 nanometers.

Sunscreens generally work in one of two ways. Particulate materials, such as zinc oxide or titanium dioxide, as mentioned above, physically block ultraviolet radiation. Chemical sunscreens, on the other hand, operate by chemically reacting upon exposure to UV radiation. Suitable sunscreens that may be included in the compositions of the invention are set forth on
15 page 582 of the CTFA Cosmetic Ingredient Handbook, Second Edition, 1992, as well as U.S. Patent No. 5,620,965, both of which are hereby incorporated by reference. Further examples of chemical and physical sunscreens include those set forth below.

(a). UVA Chemical Sunscreens

The term "UVA sunscreen" means a chemical compound that blocks UV radiation in the
20 wavelength range of about 320 to 400 nm. Preferred UVA sunscreens are dibenzoylmethane compounds having the general formula:



10 wherein R_1 is H, OR and NRR wherein each R is independently H, C_{1-20} straight or branched chain alkyl; R_2 is H or OH; and R_3 is H, C_{1-20} straight or branched chain alkyl.

Preferred is where R_1 is OR where R is a C_{1-20} straight or branched alkyl, preferably methyl; R_2 is H; and R_3 is a C_{1-20} straight or branched chain alkyl, more preferably, butyl.

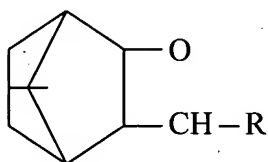
Examples of suitable UVA sunscreen compounds of this general formula include 4-
 15 methyldibenzoylmethane, 2-methyldibenzoylmethane, 4-isopropyldibenzoylmethane, 4-tert-butyldibenzoylmethane, 2,4-dimethyldibenzoylmethane, 2,5-dimethyldibenzoylmethane, 4,4'-diisopropylbenzoylmethane, 4-tert-butyl-4'-methoxydibenzoylmethane, 4,4'-diisopropylbenzoylmethane, 2-methyl-5-isopropyl-4'-methoxydibenzoylmethane, 2-methyl-5-tert-butyl-4'-methoxydibenzoylmethane, and so on. Particularly preferred is 4-tert-butyl-4'-
 20 methoxydibenzoylmethane, also referred to as Avobenzone. Avobenzone is commercial available from Givaudan-Roure under the trademark Parsol 1789, and Merck & Co. under the tradename Eusolex 9020.

The claimed compositions may contain from about 0.001-20% , preferably 0.005-5%, more preferably about 0.005-3% by weight of the composition of UVA sunscreen. In one
 25 preferred embodiment of the invention the UVA sunscreen is Avobenzone, and it is present at not greater than about 3% by weight of the total composition.

(b). UVB Chemical Sunscreens

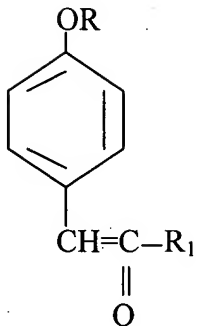
The term "UVB sunscreen" means a compound that blocks UV radiation in the wavelength range of from about 290 to 320 nm. A variety of UVB chemical sunscreens exist including α -cyano- β,β -diphenyl acrylic acid esters as set forth in U.S. Patent No. 3,215,724, which is hereby incorporated by reference in its entirety. Particularly preferred is Octocrylene, which is 2-ethylhexyl 2-cyano-3,3-diphenylacrylate. Preferred is where the composition contains no more than about 10% by weight of the total composition of octocrylene. Suitable amounts range from about 0.001-10% by weight. Octocrylene may be purchased from BASF under the tradename Uvinul N-539.

Other suitable sunscreens include benzylidene camphor derivatives as set forth in U.S. Patent No. 3,781,417, which is hereby incorporated by reference in its entirety. Such benzylidene camphor derivatives have the general formula:



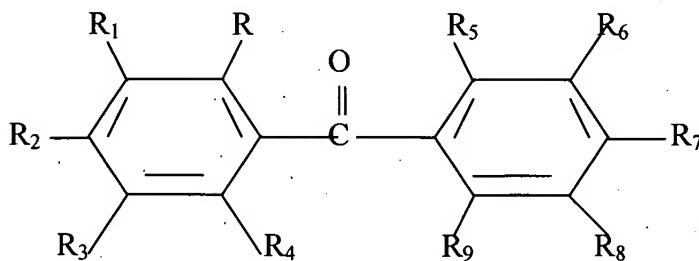
wherein R is p-tolyl or styryl, preferably styryl. Particularly preferred is 4-methylbenzylidene camphor, which is a lipid soluble UVB sunscreen compound sold under the tradename Eusolex 6300 by Merck.

Also suitable are cinnamate derivatives having the general formula:



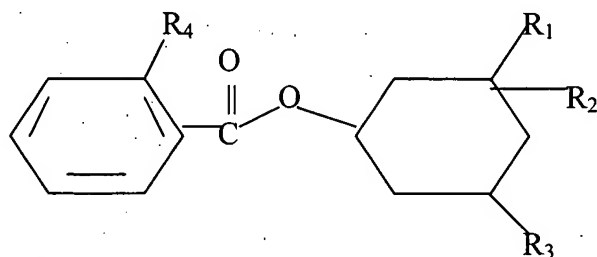
wherein R and R₁ are each independently a C₁₋₂₀ straight or branched chain alkyl. Preferred is where R is methyl and R₁ is a branched chain C₁₋₁₀, preferably C₈ alkyl. The preferred compound is ethylhexyl methoxycinnamate, also referred to as Octoxinate or octyl methoxycinnamate. The compound may be purchased from Givaudan Corporation under the tradename Parsol MCX, or BASF under the tradename Uvinul MC 80. Also suitable are mono-, di-, and triethanolamine derivatives of such methoxy cinnamates including diethanolamine methoxycinnamate. Cinoxate, the aromatic ether derivative of the above compound is also acceptable. If present, the Cinoxate should be found at nor more than about 3% by weight of the total composition.

Also suitable as the UVB screening agents are various benzophenone derivatives having the general formula:



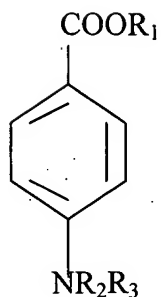
R through R₉ are each independently H, OH, NaO₃S, SO₃H, SO₃Na, Cl, R", OR" where R" is C₁-
20 straight or branched chain alkyl. Examples of such compounds include Benzophenone 1, 2, 3,
4, 5, 6, 7, 8, 9, 10, 11, and 12. Particularly preferred is where the benzophenone derivative is
5 Benzophenone 3 (also referred to as Oxybenzone) and Benzophenone 4 (also referred to as
Sulisobenzzone), Benzophenone 5 (Sulisobenzzone Sodium), and the like. Most preferred is
Benzophenone 3.

Also suitable are certain menthyl salicylate derivatives having the general formula:



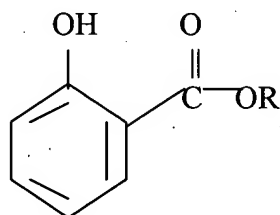
wherein R₁, R₂, R₃, and R₄ are each independently H, OH, NH₂, or C₁-₂₀ straight or branched
chain alkyl. Particularly preferred is where R₁, R₂, and R₃ are methyl and R₄ is hydroxyl or NH₂,
the compound having the name homomenthyl salicylate (also known as Homosalate) or menthyl
anthranilate. Homosalate is available commercially from Merck under the tradename Eusolex
20 HMS and menthyl anthranilate is commercially available from Haarmann & Reimer under the
tradename Heliopan. If present, the Homosalate should be found at no more than about 15% by
weight of the total composition.

Various amino benzoic acid derivatives are suitable UVB absorbers including those
having the general formula:



Wherein R_1 , R_2 , and R_3 are each independently H, C_{1-20} straight or branched chain alkyl which may be substituted with one or more hydroxy groups. Particularly preferred is wherein R_1 is H or C_{1-8} straight or branched alkyl, and R_2 and R_3 are H, or C_{1-8} straight or branched chain alkyl. Particularly preferred are PABA, ethyl hexyl dimethyl PABA (Padimate O), ethyldihydroxypropyl PABA, and the like. If present Padimate O should be found at no more than about 8% by weight of the total composition.

Salicylate derivatives are also acceptable UVB absorbers. Such compounds have the general formula:



wherein R is a straight or branched chain alkyl, including derivatives of the above compound formed from mono-, di-, or triethanolamines. Particular preferred are octyl salicylate, TEA-salicylate, DEA-salicylate, and mixtures thereof.

Generally, the amount of the UVB chemical sunscreen present may range from about 0.001-45%, preferably 0.005-40%, more preferably about 0.01-35% by weight of the total composition.

(c). Physical Sunscreens

5 The composition may also contain one or more physical sunscreens. The term "physical sunscreen" means a material that is generally particulate in form that is able to block UV rays by forming an actual physical block on the skin. Examples of particulates that serve as solid physical sunblocks include titanium dioxide, zinc oxide and the like in particle sizes ranging from about 0.001-50 microns, preferably less than 1 micron.

8. Vitamins and Antioxidants

10 The compositions of the invention may contain vitamins and/or coenzymes, as well as antioxidants. If so, 0.001-10%, preferably 0.01-8%, more preferably 0.05-5% by weight of the total composition are suggested. Suitable vitamins include ascorbic acid and derivatives thereof, the B vitamins such as thiamine, riboflavin, pyridoxin, and so on, as well as coenzymes such as
15 thiamine pyrophosphate, flavin adenin dinucleotide, folic acid, pyridoxal phosphate, tetrahydrofolic acid, and so on. Also Vitamin A and derivatives thereof are suitable. Examples are Vitamin A palmitate, acetate, or other esters thereof, as well as Vitamin A in the form of beta carotene. Also suitable is Vitamin E and derivatives thereof such as Vitamin E acetate, nicotinate, or other esters thereof. In addition, Vitamins D and K are suitable.

20 Suitable antioxidants are ingredients which assist in preventing or retarding spoilage. Examples of antioxidants suitable for use in the compositions of the invention are potassium sulfite, sodium bisulfite, sodium erythrobate, sodium metabisulfite, sodium sulfite, propyl gallate, cysteine hydrochloride, butylated hydroxytoluene, butylated hydroxyanisole, and so on.

9. Humectants

If desired, the compositions of the invention comprise about 0.01-30%, preferably about 0.5-25%, more preferably about 1-20% by weight of the total composition of one or more humectants. Suitable humectants include di- or polyhydric alcohols such as glycols, sugars, and similar materials. Suitable glycols include alkylene glycols such as propylene, ethylene, or butylene glycol; or polymeric alkylene glycols such as polyethylene and polypropylene glycols, including PEG 4-240, which are polyethylene glycols having from 4 to 240 repeating ethylene oxide units. Suitable sugars, some of which are also polyhydric alcohols, are also suitable humectants. Examples of such sugars include glucose, fructose, honey, hydrogenated honey, inositol, maltose, mannitol, maltitol, sorbitol, sucrose, xylitol, xylose, and so on.

10. Other Botanical Extracts

It may be desirable to include one or more additional botanical extracts in the compositions. If so, suggested ranges are from about 0.0001 to 10%, preferably about 0.0005 to 8%, more preferably about 0.001 to 5% by weight of the total composition. Suitable botanical extracts include extracts from plants (herbs, roots, flowers, fruits, seeds) such as flowers, fruits, vegetables, and so on, including acacia (dealbata, farnesiana, senegal), acer saccharinum (sugar maple), acidopholus, acorus, aesculus, agaricus, agave, agrimonia, algae, aloe, citrus, brassica, cinnamon, orange, apple, blueberry, cranberry, peach, pear, lemon, lime, pea, seaweed, green tea, chamomile, willowbark, mulberry, poppy, and those set forth on pages 1646 through 1660 of the CTFA Cosmetic Ingredient Handbook, Eighth Edition, Volume 2.

11. Water Soluble Gellants

If the composition is in the emulsion form, it may be desirable to include other water soluble gellants in the water phase of the composition to provide thickening. Such gellants may

be included a range of about 0.1-20%, preferably about 1-18%, more preferably about 2-10% by weight of the total composition is suggested, if present. Suitable gellants include soaps, i.e. salts of water insoluble fatty acids with various bases. Examples of soaps include the aluminum, calcium, magnesium, potassium, sodium, or zinc salts of C₆₋₃₀, preferably C₁₀₋₂₂ fatty acids.

5 Also suitable are hydrocolloids such as gellan gum, gum arabic, carrageenan, and those set forth in U.S. Patent No. 6,197,319 which is hereby incorporated by reference in its entirety.

12. Preservatives

The composition may contain 0.001-8%, preferably 0.01-6%, more preferably 0.05-5% by weight of the total composition of preservatives. A variety of preservatives are suitable,
10 including such as benzoic acid, benzyl alcohol, benzylhemiformal, benzylparaben, 5-bromo-5-nitro-1,3-dioxane, 2-bromo-2-nitropropane-1,3-diol, butyl paraben, phenoxyethanol, methyl paraben, propyl paraben, diazolidinyl urea, calcium benzoate, calcium propionate, captan, chlorhexidine diacetate, chlorhexidine digluconate, chlorhexidine dihydrochloride, chloroacetamide, chlorobutanol, p-chloro-m-cresol, chlorophene, chlorothymol, chloroxylonol,
15 m-cresol, o-cresol, DEDM Hydantoin, DEDM Hydantoin dilaurate, dehydroacetic acid, diazolidinyl urea, dibromopropamide diisethionate, DMDM Hydantoin, and all of those disclosed on pages 570 to 571 of the CTFA Cosmetic Ingredient Handbook, Second Edition, 1992, which is hereby incorporated by reference.

13. Emulsion Stabilizers

20 If the composition of the invention is in the emulsion form, it may be desirable to incorporate one or more emulsion stabilizers in the composition. If so, suggested ranges are about 0.0001-5%, preferably about 0.0005-3%, more preferably about 0.001-2% by weight of the

total composition. Suitable emulsion stabilizers include salts of alkali or alkaline earth metal chlorides or hydroxides, such as sodium chloride, potassium chloride, and the like.

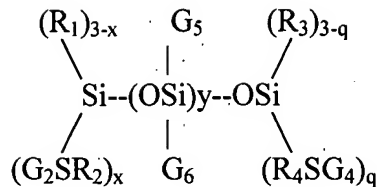
14. Other Film Forming Polymers

It may be desired for the cosmetic composition to contain one or more additional film forming polymers. Such polymers may be silicones or polymers with repeating organic moieties. If present, such film forming polymers are found in ranges of about 0.001-50%, preferably about 0.01-45%, more preferably about 0.1-20% by weight of the total composition. Such film forming polymers may be present in the form of dispersed or solvated particles in water, or in other non-aqueous solvents such as paraffinic hydrocarbons, silicone oils, or organic oils. Examples of such film forming polymers include those set forth below.

(a). Copolymers of Silicone and Ethylenically Unsaturated Monomers

One type of film forming polymer that may be used in the compositions of the invention is obtained by reacting silicone moieties with ethylenically unsaturated monomers. The resulting copolymers may be graft or block copolymers. The term "graft copolymer" is familiar to one of ordinary skill in polymer science and is used herein to describe the copolymers which result by adding or "grafting" polymeric side chain moieties (i.e. "grafts") onto another polymeric moiety referred to as the "backbone". The backbone may have a higher molecular weight than the grafts. Thus, graft copolymers can be described as polymers having pendant polymeric side chains, and which are formed from the "grafting" or incorporation of polymeric side chains onto or into a polymer backbone. The polymer backbone can be a homopolymer or a copolymer. The graft copolymers are derived from a variety of monomer units.

One type of polymer that may be used as the film forming polymer is a vinyl-silicone graft or block copolymer having the formula:



wherein G_5 represents monovalent moieties which can independently be the same or different selected from the group consisting of alkyl, aryl, aralkyl, alkoxy, alkylamino, fluoroalkyl, hydrogen, and -ZSA; A represents a vinyl polymeric segment consisting essentially of a polymerized free radically polymerizable monomer, and Z is a divalent linking group such as C_{1-10} alkylene, aralkylene, arylene, and alkoxyalkylene, most preferably Z is methylene or propylene.

G_6 is a monovalent moiety which can independently be the same or different selected from the group consisting of alkyl, aryl, aralkyl, alkoxy, alkylamino, fluoroalkyl, hydrogen, and -ZSA;

G_2 comprises A;

G_4 comprises A;

R_1 is a monovalent moiety which can independently be the same or different and is selected from the group consisting of alkyl, aryl, aralkyl, alkoxy, alkylamino, fluoroalkyl, hydrogen, and hydroxyl; but preferably C_{1-4} alkyl or hydroxyl, and most preferably methyl.

R_2 is independently the same or different and is a divalent linking group such as C_{1-10} alkylene, arylene, aralkylene, and alkoxyalkylene, preferably C_{1-3} alkylene or C_{7-10} aralkylene, and most preferably $-CH_2-$ or 1,3-propylene, and

R_3 is a monovalent moiety which is independently alkyl, aryl, aralkyl, alkoxy, alkylamino, fluoroalkyl, hydrogen, or hydroxyl, preferably C_{1-4} alkyl or hydroxyl, most preferably methyl;

Y is a divalent linking group which is alkylene, arylene, alkarylene, and aralkylene of 1 to 30 carbon atoms which may incorporate ester, amide, urethane, or urea groups,

n is zero or 1;

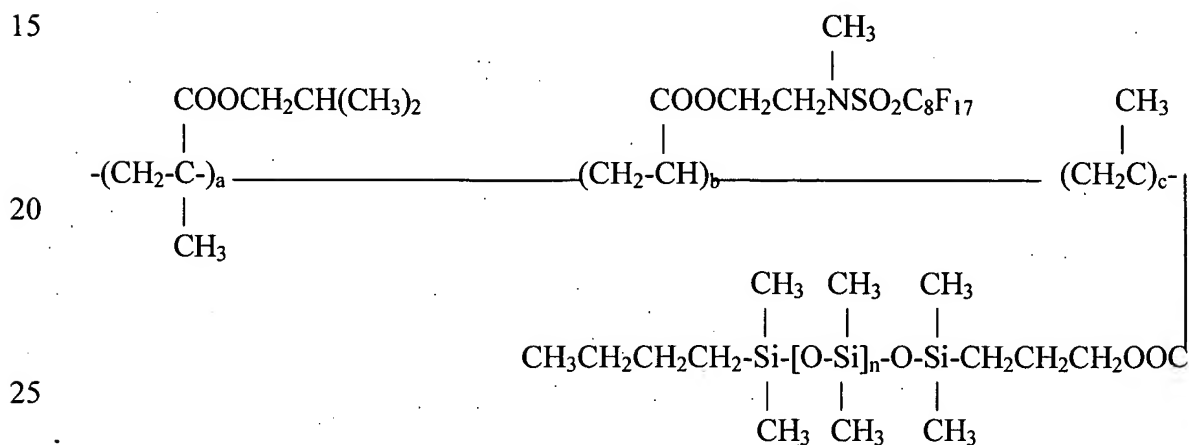
m is an integer of from 1 to 3,

5 R is hydrogen, C₁₋₄ alkyl, aryl, or alkoxy,

Z is a monovalent siloxane polymeric moiety; and

D is at least one free radically polymerizable acrylate or methacrylate copolymer.

Such polymers and their manufacture are disclosed in U.S. Pat. Nos. 5,209,924 and 4,972,037, which are hereby incorporated by reference. More specifically, the preferred
10 polymer is a combination of A, C, and D monomers wherein A is a polymerizable acrylic or methacrylic ester of a fluoroalkylsulfonamido alcohol, and where D is a methacrylic acid ester of a C₁₋₂ straight or branched chain alcohol, and C is as defined above. Most preferred is a polymer having moieties of the general formula:



wherein each of a, b, c, and n have a value in the range of 1-100,000, and the terminal groups are selected from the group consisting of a C₁₋₂₀ straight or branched chain alkyl, aryl, and alkoxy and

30 the like. These polymers may be purchased from Minnesota Mining and Manufacturing

Company under the tradenames "Silicone Plus" polymers. Most preferred is poly(isobutyl methacrylate -co- methyl FOSEA) -g- poly(dimethylsiloxane) which is sold under the tradename SA 70-5 IBMMF or Polysilicone 7.

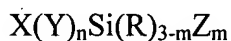
Another suitable silicone acrylate copolymer is a polymer having a vinyl, methacrylic, or acrylic polymeric backbone with pendant siloxane groups. Such polymers as disclosed in U.S. Pat. Nos. 4,693,935, 4,981,903, 4,981,902, and which are hereby incorporated by reference.

Preferably, these polymers are comprised of A, C, and optionally B monomers wherein:

A is at least one free radically polymerizable vinyl, methacrylate, or acrylate monomer;

B, when present, is at least one reinforcing monomer copolymerizable with A,

C is a monomer having the general formula:



wherein:

X is a vinyl group copolymerizable with the A and B monomers;

Y is a divalent linking group;

n is zero or 1;

m is an integer of from 1 to 3;

R is hydrogen, C₁₋₁₀ alkyl, substituted or unsubstituted phenyl, C₁₋₁₀ alkoxy; and

Z is a monovalent siloxane polymeric moiety.

Examples of A monomers are lower to intermediate methacrylic acid esters of C₁₋₁₂ straight or branched chain alcohols, styrene, vinyl esters, vinyl chloride, vinylidene chloride, acryloyl monomers, and so on.

The B monomer, if present, is a polar acrylic or methacrylic monomer having at least one hydroxyl, amino, or ionic group (such as quaternary ammonium, carboxylate salt, sulfonic acid

salt, and so on).

The C monomer is as above defined.

Examples of other suitable copolymers that may be used herein, and their method of manufacture, are described in detail in U.S. Pat. No. 4,693,935, Mazurek, U.S. Pat. No. 4,728,571, and Clemens et al., both of which are incorporated herein by reference. Additional grafted polymers are also disclosed in EPO Application 90307528.1, published as EPO Application 0 408 311, U.S. Pat. No. 5,061,481, Suzuki et al., U.S. Pat. No. 5,106,609, Bolich et al., U.S. Pat. No. 5,100,658, Bolich et al., U.S. Pat. No. 5,100,657, Ansher-Jackson, et al., U.S. Pat. No. 5,104,646, Bolich et al., U.S. Pat. No. 5,618,524, issued Apr. 8, 1997, all of which are incorporated by reference herein in their entirety.

(b). Polymers from Ethylenically Unsaturated Monomers

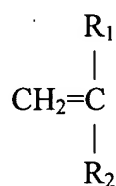
Also suitable for use as film forming polymers are polymers made by polymerizing one or more ethylenically unsaturated monomers. The final polymer may be a homopolymer, copolymer, terpolymer, or graft or block copolymer, and may contain monomeric units such as acrylic acid, methacrylic acid or their simple esters, styrene, ethylenically unsaturated monomer units such as ethylene, propylene, butylene, etc., vinyl monomers such as vinyl chloride, styrene, and so on.

Preferred are polymers containing one or more monomers which are esters of acrylic acid or methacrylic acid, including aliphatic esters of methacrylic acid like those obtained with the esterification of methacrylic acid or acrylic acid with an aliphatic alcohol of 1 to 30, preferably 2 to 20, more preferably 2 to 8 carbon atoms. If desired, the aliphatic alcohol may have one or more hydroxy groups. Also suitable are methacrylic acid or acrylic acid esters esterified with moieties containing alicyclic or bicyclic rings such as cyclohexyl or isobornyl, for example.

The ethylenically unsaturated monomer may be mono-, di-, tri-, or polyfunctional as regards the addition-polymerizable ethylenic bonds. A variety of ethylenically unsaturated monomers are suitable.

Examples of suitable monofunctional ethylenically unsaturated monomers include those of the formula:

I.



wherein R_1 is H, a C_{1-30} straight or branched chain alkyl, aryl, aralkyl; R_2 is a pyrrolidone, a C_{1-30} straight or branched chain alkyl, or a substituted or unsubstituted aromatic, alicyclic, or bicyclic ring where the substituents are C_{1-30} straight or branched chain alkyl, or COOM wherein M is H, a C_{1-30} straight or branched chain alkyl, pyrrolidone, or a substituted or unsubstituted aromatic, alicyclic, or bicyclic ring where the substituents are C_{1-30} straight or branched chain alkyl which may be substituted with one or more hydroxyl groups, or $[(CH_2)_mO]_nH$ wherein m is 1-20, and n is 1-200.

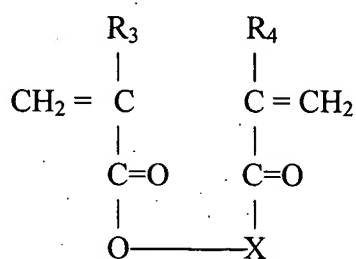
Preferably, the monofunctional ethylenically unsaturated monomer is of Formula I, above, wherein R_1 is H or a C_{1-30} alkyl, and R_2 is COOM wherein M is a C_{1-30} straight or branched chain alkyl which may be substituted with one or more hydroxy groups.

More preferably, R_1 is H or CH_3 , and R_2 is COOM wherein M is a C_{1-10} straight or branched chain alkyl which may be substituted with one or more hydroxy groups. In the preferred embodiment of the invention, the monofunctional ethylenically unsaturated monomer

is a mixture of monomers of Formula I where in one monomer R_1 is H or CH_3 and R_2 is COOM where M is a C_{1-10} alkyl, and where in the second monomer R_1 is H or CH_3 , and R_2 is COOM where M is a C_{1-10} alkyl substituted with one or more hydroxy groups.

Di-, tri- and polyfunctional monomers, as well as oligomers, of the above monofunctional monomers may also be used to form the polymer. Suitable difunctional monomers include those having the general formula:

II.



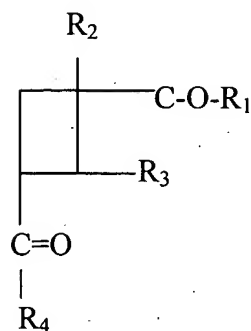
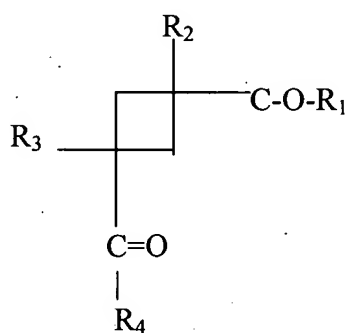
wherein R_3 and R_4 are each independently H, a C_{1-30} straight or branched chain alkyl, aryl, or aralkyl; and X is $[(CH_2)_xO_y]_z$ wherein x is 1-20, and y is 1-20, and z is 1-100. Particularly preferred are difunctional acrylates and methacrylates, such as the compound of formula II above wherein R_3 and R_4 are CH_3 and X is $[(CH_2)_xO_y]_z$ wherein x is 1-4; and y is 1-6; and z is 1-10.

Trifunctional and polyfunctional monomers are also suitable for use in the polymerizable monomer to form the polymer used in the compositions of the invention. Examples of such monomers include acrylates and methacrylates such as trimethylolpropane trimethacrylate or trimethylolpropane triacrylate.

The polymers can be prepared by conventional free radical polymerization techniques in which the monomer, solvent, and polymerization initiator are charged over a 1-24 hour period of time, preferably 2-8 hours, into a conventional polymerization reactor in which the constituents are heated to about 60-175° C., preferably 80-100° C. The polymers may also be made by

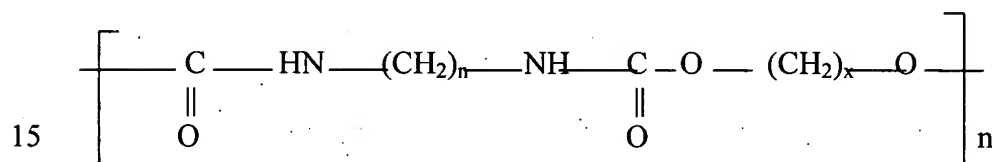
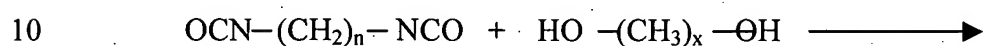
emulsion polymerization or suspension polymerization using conventional techniques. Also anionic polymerization or Group Transfer Polymerization (GTP) is another method by which the copolymers used in the invention may be made. GTP is well known in the art and disclosed in U.S. Patent Nos. 4,414,372; 4,417,034; 4,508,880; 4,524,196; 4,581,428; 4,588,795; 4,598,161; 4,605,716; 4,605,716; 4,622,372; 4,656,233; 4,711,942; 4,681,918; and 4,822,859; all of which are hereby incorporated by reference.

Also suitable are polymers formed from the monomer of Formula I, above, which are cyclized, in particular, cycloalkylacrylate polymers or copolymers having the following general formulas:



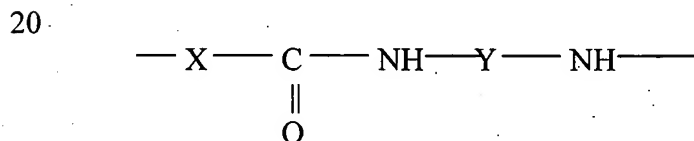
wherein R₁, R₂, R₃, and R₄ are as defined above. Typically such polymers are referred to as cycloalkylacrylate polymers. Such polymers are sold by Phoenix Chemical, Inc. under the tradename Giovarez AC-5099M. Giovarez has the chemical name isododecane acrylates copolymer and the polymer is solubilized in isododecane. The monomers mentioned herein can be polymerized with various types of organic groups such as propylene glycol, isocyanates, amides, etc.

One type of organic group that can be polymerized with the above monomers includes a urethane monomer. Urethanes are generally formed by the reaction of polyhydroxy compounds with diisocyanates, as follows:



wherein x is 1-1000.

Another type of monomer that may be polymerized with the above comprise amide groups, preferably having the the following formula:



25 wherein X and Y are each independently linear or branched alkylene having 1-40 carbon atoms, which may be substituted with one or more amide, hydrogen, alkyl, aryl, or halogen substituents.

Another type of organic monomer may be alpha or beta pinenes, or terpenes, abietic acid, and the like.

Suitable silicone polymers include silicone esters set forth in U.S. Patent No. 5,725,845 which is hereby incorporated by reference in its entirety. Other polymers that can enhance adhesion to skin include silicone esters comprising units of the general formula $R_aR_b^E\text{SiO}_{[4-(a+b)/2]}$ or $R^{13}_xR^E_y\text{SiO}_{1/2}$ wherein R and R^{13} are each independently an organic radical such as alkyl, cycloalkyl, or aryl, or, for example, methyl, ethyl, propyl, hexyl, octyl, decyl, aryl, cyclohexyl, and the like, a is a number ranging from 0 to 3, b is a number ranging from 0 to 3, a+b is a number ranging from 1 to 3, x is a number from 0 to 3, y is a number from 0 to 3 and the sum of x+y is 3, and wherein R^E is a carboxylic ester containing radical. Preferred R_E radicals are those wherein the ester group is formed of one or more fatty acid moieties (e.g. of about 2, often about 3 to 10 carbon atoms) and one or more aliphatic alcohol moieties (e.g. of about 10 to 30 carbon atoms). Examples of such acid moieties include those derived from branched-chain fatty acids such as isostearic, or straight chain fatty acids such as behenic. Examples of suitable alcohol moieties include those derived from monohydric or polyhydric alcohols, e.g. normal alkanols such as n-propanol and branched-chain etheralkanols such as (3,3,3-trimethylolpropoxy)propane. Preferably the ester subgroup (i.e. the carbonyloxy radical) will be linked to the silicon atom by a divalent aliphatic chain that is at least 2 or 3 carbon atoms in length, e.g. an alkylene group or a divalent alkyl ether group. Most preferably that chain will be part of the alcohol moiety, not the acid moiety. Silicone esters having the above formula are disclosed in U.S. patent no. 4,725,658 and U.S. patent no. 5,334,737, which are hereby incorporated by reference. Preferred silicone esters are the liquid siloxy silicates disclosed in U.S. patent no. 5,334,737, e.g. diisostearoyl trimethylolpropane siloxysilicate (prepared in Examples 9 and 14 of this patent), and dilauroyl trimethylolpropane siloxy silicate (prepared in Example 5 of the patent), which are commercially available from General Electric under the tradenames SF 1318 and SF 1312, respectively.

Silicone gums or other types of silicone solids may be also used in the compositions of the invention. Examples of silicone gums include those set forth in U.S. Patent No.6,139,823, which is hereby incorporated by reference. Preferred gums have a viscosity ranging from 600,000 to 1,000,000 centipoise at 25° C.

5 (c). Natural Polymers

Also suitable for use are one or more naturally occurring polymeric materials such as resinous plant extracts including such as rosin, shellac, and the like.

II. Forms of the Cosmetic Composition

A. Foundation Makeup, Color Cosmetics

10 The cosmetic compositions may be in the form of foundation makeup or color cosmetics such as eyeshadow, blush, concealer, eyeliner, mascara, brow color; and in the liquid, cream, solid, or stick form. Suitable foundation makeup compositions may be water-in-oil or oil-in-water emulsions. Such compositions generally comprise about :

- 0.001-80% of the silicone resin polymer,
- 15 0.5-95% water,
- 0.5-25% particulate matter,
- 0.01-20% surfactant, and
- 0.1-95% nonvolatile or volatile oil.

In addition, these composition may further contain ingredients selected from the group of
20 humectants, preservatives, gellants, and all of the ingredients as set forth above in the ranges set forth herein.

Various anhydrous color cosmetic products may also be suitable, such as blush, powder, lipsticks, eyeshadows, and the like. Such anhydrous color cosmetic compositions may generally comprise about:

0.001-80% of the silicone resin polymer,

0.1-99% oil,

0.1-80% particulate matter; and optionally

0.001-50% thickening agent or wax.

The compositions may additionally contain the various other ingredients set forth above and in the ranges taught.

Preferably, the compositions are in the form of a lipcolor or lipstick, which may be a composition for coloring the lips that is in liquid, semi-solid, or solid form.

Alternatively, the composition may be in the form of a base lip color, which is a lip color applied to the lips as a basecoat to provide color, followed by application of a separate gloss coat which comprises one or more oils or waxes that provide shine, moisturization, or similar benefits to the layers applied to the lips. Examples of such lip compositions and topcoats are disclosed in U.S. Patent Application No. 2002/0159960, entitled "Method for Improving the Properties of Transfer Resistant Lip Compositions and Related Compositions and Articles", claiming priority from provisional application no. 60/271,849, filed February 27, 2001; which is hereby incorporated by reference in its entirety.

B. Lotions, Creams, Gels, and Sunscreens

The cosmetic compositions of the invention may be in the form of lotions, gels or sunscreens. Suitable skin care lotions and creams are in the emulsion form, and may be water-

in-oil or oil-in-water emulsions, preferably oil-in-water emulsions. Creams, lotions, and/or may contain the following ranges of ingredients:

about 0.001-80% of the silicone resin polymer,

about 0.1-90% oil, and

5 about 0.01-20% surfactant.

C. Skin and Hair Cleansing and Conditioning Compositions

Skin and hair cleansing and conditioning compositions such as facial cleansers, shampoos, hair conditioners and the like are also suitable cosmetic compositions in accordance with the invention.

10 Generally skin and hair cleansing compositions comprise about:

0.001-80% of the silicone resin polymer,

1-95% water, and

0.1-40% surfactant, preferably an anionic, amphoteric, or zwitterionic surfactant.

0.01-40% oil.

15 Suitable hair conditioner compositions comprise:

0.001-80% of a silicone resin polymer,

0.1-20% cationic surfactant,

0.1-30% fatty alcohol,

0.001-10% nonionic surfactant, and

20 5-95% water.

Suitable cationic and nonionic surfactants are as mentioned herein. Examples of suitable fatty alcohols include those having the general formula R-OH, wherein R is a

C₆₋₃₀ straight or branched chain, saturated or unsaturated alkyl.

D. Nail Enamel Compositions

The cosmetic compositions of the invention may also be in the form of nail enamel compositions. Such compositions generally comprise:

5 0.001-80% of the silicone resin polymer,
 0.01-80% solvent,
 0.001-40% particulate matter, and
 optionally 0.01-40% of one or more polymers such as cellulosic polymers, acrylate
polymers, and the like.

10 Suitable solvents include acetone, alkyl acetates such as ethyl acetate butyl acetate and
the like, alkyl ethers such as propylene glycol monomethyl ether, and the like.

III. The Method

The invention is directed to improving the finish of a cosmetic composition by
formulating the composition with a silicone resin comprised of M units in combination with Q or
15 T units or both, wherein the number of M units in the polymer is greater than the number of Q or
T units or combination thereof. The silicone resin polymer will cause the cosmetic composition
to exhibit an improved finish when applied to skin, lips, or hair. The term "improved finish"
means that the finish will exhibit a desirable property such as increased shine (or gloss),
improved wear, improved comfort, and in some cases, transfer resistance. Particularly preferred
20 is where the silicone resin polymer of the invention improves the finish by increasing the shine
of the finish. Most preferred is where the finish is a shiny, transfer resistant finish, particularly
with respect to lip color.

The invention will be further described in connection with the following examples which are set forth for the purposes of illustration only.

EXAMPLE 1

A semi-solid lip color composition was prepared according to the following formula:

5		<u>w/w%</u>
	Silicone acrylate copolymer*	64.2
	MQ Resin**	18.3
	Dimethicone, 60,000 centistokes	13.0
	Polyethylene wax	1.8
10	Pigments (mica, iron oxides, pearl, dimethicone)	6.55
	Isododecane	QS 100

* Shin Etsu X-22-8238, 40% solids in isododecane

** Shin Etsu X-21-5561, 65% solids in isododecane

15 EXAMPLE 2

A semi-solid composition suitable for use as lipcolor, blush, eyecolor, or the like was prepared according to the following formula:

		<u>w/w%</u>
	Silicone acrylate copolymer*	57.50
20	MQ Resin**	20.50
	Quaternium 18 hectorite	7.00
	Dimethicone, 60,000 centistokes	13.0
	Polyethylene wax	1.8
	Pigments	6.55

Isododecane

QS 100

* Shin Etsu X-22-8238, 40% solids in isododecane

** Shin Etsu X-21-5561, 65% solids in isododecane

5

EXAMPLE 3

Semi-solid compositions suitable for use as lipcolor, blush, eyecolor, or the like were prepared according to the following formula:

		<u>w/w%</u>				
		<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
10	Silicone acrylate copolymer*	57.50	57.50	57.50	57.50	57.50
	MQ Resin**	20.50	20.50	20.50	20.50	20.50
	Quaternium 18 hectorite	7.00	7.00	7.00	7.00	7.00
	Dimethicone, 60,000 centistokes	13.0	13.00	13.00	13.00	13.00
	Polyethylene wax	1.80	1.80	1.80	1.80	1.80
15	Pigments (Red #6, iron oxides)	6.55	6.55	6.55	6.55	6.55
	Octyl isononanoate	----	2.50	----	----	----
	Dibutyl adipate	----	----	2.50	----	----
	Glyceryl trioctanoate	----	----	----	2.50	----
	Pentaerythrityl tetraoctanoate	----	----	----	----	2.50
20	Isododecane	QS 100-----				

* Shin Etsu X-22-8238, 40% solids in isododecane

** Shin Etsu X-21-5561, 65% solids in isododecane

25 The compositions were prepared by combining the ingredients and mixing well, then pouring into containers.

While the invention has been described in connection with the preferred embodiment, it is not intended to limit the scope of the invention to the particular form set forth but, on the contrary, it is intended to cover such alternatives, modifications, and equivalents as may be included within the spirit and scope of the invention as defined by the appended claims.